ALKYLBENZENE/POLYOL ESTER BLENDS FOR USE IN AIR CONDITIONING SYSTEMS

This application claims the benefit of Provisional Patent Application No. 60/434,845, filed on December 19, 2002.

Background of the Invention

Residential and commercial air conditioning applications account for a substantial segment of the air conditioning market worldwide. Historically, residential and commercial air conditioning units used chlorine-based refrigerants such as refrigerant R12 and R22. These refrigerants, however, are being phased out due to Montreal Protocol regulations that require new refrigerants to be chlorine free due to the deleterious effect chlorine has on the ozone layer.

Today's refrigerants must be chlorine-free and are hydrofluorocarbon (HFC) refrigerants. Thus, one of the replacements for R22 in existing refrigeration systems is HFC R407c which is a blend of R32, R125 and R134a HFC refrigerants at 23, 25 and 52% wt respectively. There is a problem, however, in finding lubricants suitable for fluorine-only refrigerants.

The lubricants currently used with R22, mineral oil based and alkylbenzene based, are not completely miscible or soluble with R407C across the temperature range required for effective use. This is likely to cause problems with (a) lubricant return to the compressor from the system; and (b) fouling of heat transfer surfaces, e.g. evaporator / condenser. But, alkylbenzene based lubricants offer reduced cost and increased film surface tension to the lubricant that provides wear benefits for rotary compressor applications.

Polyol esters, although suitable in terms of miscibility and compatibility with HFC refrigerants, are not satisfactory for all rotary compressor applications. Particular wear problems are observed due to the demands of this type of compressor. The polyol ester products are also high in cost relative to traditional mineral oil or alkylbenzene based lubricants.

Thus, there is a demand for low cost alternatives to polyol esters for these applications.

Summary of the Invention

Alkylbenzene/polyol ester blends with a high proportion of alkylbenzene offer a reduced cost alternative (compared to polyol esters) with sufficient HFC refrigerant

solvency to operate satisfactorily. By mixing alkylbenzene ("AB") and polyol ester ("POE") lubricants, of similar viscosity, applicants obtain a product with beneficial properties from each component.

The POE component acts as a solvent and dissolves refrigerant into the lubricant phase. The ability to dissolve refrigerant into a lubricant phase consisting of AB/POE will reduce the viscosity and promote oil return to the compressor and reduce heat transfer device fouling. The AB lubricant component provides increased film surface tension to the lubricant which reduces wear in rotary compressor applications thus contributing both wear and cost benefits.

AB/POE blends having a ratio of 60-80 wt% alkylbenzene to 20-40 wt% polyol ester provide the most suitable overall balance between cost, solubility and physical and wear characteristics.

The present invention is thus directed to a refrigerator oil composition comprising about 60-80 wt% alkylbenzene and 20-40 wt% polyol esters for use with HFC refrigerants such as R407C, R410A and R507.

Brief Description of the Drawings

FIGURES 1-4 are phase composition graphs for blends of alkylbenzene and polyol ester ranging from 100 wt% alkylbenzene to 50 wt% alkylbenzene.

FIGURES 5-8 are graphs of the friction coefficient for two viscosity grades of 80/20 and 70/30 alkylbenzene/polyol ester blends during the SRV EP Test.

FIGURES 9-12 are graphs of the friction coefficient for two viscosity grades of 80/20 and 70/30 alkylbenzene/polyol ester blends during the SRV 5AE Test.

FIGURES 13-17 are lubricant profiles comparing the properties of a 70/30 (ISO 32) blend of alkylbenzene/polyol ester with 100% polyol ester lubricant.

Description of the Preferred Embodiment(s)

This invention will be further explained in detail with reference to the following preferred embodiments.

The alkylbenzene component of the refrigerator oil composition may constitute any molecular structure of alkylbenzenes of the desired viscosity.

The polyol ester component of the present refrigerator oil composition includes esters of a polyol having 2 to 6 hydroxyl groups and any linear or branched carboxylic acid having 5 to 9 carbon atoms. Specific examples of polyols include neopentyl glycol, trimethylol propane, pentaerythritol, di-trimethylol propane, di-pentaerythritol,

though preferably pentaerythritol. The carboxylic acid is preferably selected from pentanoic acid, heptanoic acid, 2-ethyl-hexanoic acid, octanoic acid, hexanoic acid, nonanoic acid, 2-methylpropionic acid, 3-methylbutanoic acid, isopentanoic acid, isononanoic acid, 3,5,5, trimethylhexanoic acid, and more preferably selected from pentanoic acid, heptanoic acid, 2-ethyl-hexanoic acid, and 3,5,5, trimethylhexanoic acid. Although there is no specific limitation imposed on the viscosity of the polyol ester used in the present invention, it is preferable to select a polyol ester having a kinematic viscosity similar to (within a range of +/- 30% at 40 Deg C) the viscosity of the selected alkylbenzene. It is also possible to blend an alkylbenzene and polyol ester of different viscosities to achieve the desired viscosity of the end product. The end product preferably has a viscosity is between 20 and 200 cSt, more preferably between 20 and 100 cSt and most preferably between 20 and 80 cSt at 40 Deg C.

The present invention also applies to blends of 60 – 80 wt% alkylbenzene and 20 – 40 wt% of polyalkylene glycol (PAG). PAG is used in about 95% of passenger vehicle and truck air conditioning systems. PAG is more costly than alkylbenzene but alkylbenzenes are not soluble in automotive air conditioning refrigerants such as R134a, R744 and R152a. Thus, as in the AB/POE blend, the PAG provides sufficient solubility and the AB provides cost benefits.

The present invention may be used in many different compressor types. Typically reciprocating, scroll, rotary, and screw compressors are used in commercial office buildings for occupant comfort cooling, whilst process cooling and refrigeration used in manufacturing would typically utilize centrifugal chillers, screw and reciprocating compressors. Automotive and truck applications typically use reciprocating, scroll or rotary compressors.

The invention described herein will be better understood by consideration of the following examples, which are offered by way of illustration and not intended to be limiting.

Examples

To test these AB/POE blends a static test method was developed to determine the effect of HFC refrigerant solubility in the lubricant blend as the ratio of AB to POE was varied.

Viscosity grades ISO 32 and ISO 68 were chosen for evaluation. Ratios of AB/POE used were from 90:10 to 50:50 (by weight).

All the blends were partially miscible with HFC refrigerant R407C and separated into two phases at the evaluated temperature. One phase was refrigerant rich and the other lubricant rich. The phase separation technique enabled the phases to be separated by a dip tube and the relative amounts of lubricant/refrigerant in each phase calculated.

Data generated on proportions of refrigerant in the lubricant phase allow viscosity calculations to be made. The theoretical viscosity of the lubricant in evaporator conditions (e.g. -20°C) can be calculated and compared to existing data for R22/mineral oil.

Example 1

Static Testing

Preliminary testing of the AB/POE mixtures was carried out on the following alkylbenzene/polyol ester blends in Table I:

Table I

	POE	ALKYLBENZENE
Viscosity	ISO 68	ISO 68
T Number	%Weight	%Weight
T66804/94	0	100
T11676/95	10	90
T11677/95	20	80
T11678/95	30	70
T65915/94	100	0
Viscosity	ISO 32	ISO 32
T Number	%Weight	%Weight
T11495/95	0	100
T11679/95	10	90
T11680/95	20	80
T11681/95	30	70
T65913/94	100	0

The ISO 68 and ISO 32 polyol esters in Example 1 are polyol esters derived from a reaction mixture of pentanoic acid and 3,5,5, trimethyl hexanoic acid with

Pentaerythritol. ISO 68 POE is derived from 18 wt% pentanoic acid and 82 wt% 3,5,5, trimethyl hexanoic acid, while ISO 32 POE is derived from 54.5 wt% pentanoic acid and 45.5 wt% 3,5,5, trimethyl hexanoic acid. The ISO 32 and 68 Alkylbenzenes used in Example 1 were Zerol 150 and Zerol 300 which are commercially available from Shrieve Chemical Company.

The lubricant blends were mixed with refrigerant R407C (at 15% oil in R407C) and observations regarding phase separation at +20°C, 0°C, and -20°C are shown in Tables II and III.

Table II

Observation of AB/POE Blends in R407C

T Number	**% ISO 32 AB**	**Observation of Phases at**		
		+20°C	**0°C**	**-20°C**
T11495/95	100	T oil clear B ref clear	T oil cloudy B ref cloudy	T oil clear B ref cloudy
T11679/95	90	T oil clear B ref hazy	T oil cloudy B ref cloudy	T oil cloudy B ref cloudy
T11680/95	80	T oil clear B ref clear	T oil clear B ref clear	T oil cloudy B ref cloudy
T11681/95	70	T oil clear B ref clear	T oil clear B ref hazy	T oil cloudy B ref hazy

Table III

T Number	**%ISO 68 AB**	**Observation of Phases at**		
		+20°C	**0°C**	**-20°C**
T66804/94	100	T oil clear B ref clear	T oil hazy B ref hazy	T oil cloudy B ref hazy
T11676/95	90	T oil clear B ref clear	T oil cloudy B ref cloudy	T oil cloudy B ref cloudy
T11677/95	80	T oil clear B ref clear	T oil hazy B ref cloudy	T oil cloudy B ref cloudy
T11678/95	70	T oil clear B ref clear	T oil cloudy B ref cloudy	T oil cloudy B ref cloudy

Key for Table II and III:

ref: Refrigerant rich phase

T: Top phase

B: Bottom phase

The preliminary observations at -20°C, 0°C and 20°C showed that the AB/POE lubricant mixture formed two phases with R407C in all cases (at 15% wt oil in R407C).

Example 2

Phase Separation and Lubricant Composition Graphs

To determine the composition of the phase in a two phase refrigerant lubricant mixture the phases need to be separated. Once separated the amount of AB, POE and HFC 407C can be calculated for each phase.

R407C with AB/POE Blend Phase Separation

Top	Contains:	Alkylbenzene, polyolester and R407C (predominantly lubricant)
Bottom	Contains:	Alkylbenzene, polyolester and R407C (predominantly refrigerant)

The mixture separates into two distinct layers and the bottom layer can be removed by a cannula (dip tube) by the following procedure:

Phase Separation Test Method

The test method uses two standard Pamasol® glass tubes and toggle valves. Tube 1 consists of a stand, glass tube, thermocouple and dip tube with standard seal fittings. Tube 2 consists of a stand, a second glass tube, thermocouple and standard seal fittings. The glass tubes are capable of withstanding high pressure, of approximately 20 Bar. Fixed into the closure of the tube is a temperature probe and a valve mechanism. The two tubes are connected by a copper pipe with toggle valves onto each tube. Tubes 1 and 2 are weighed before use.

The refrigerant/lubricant mixture is added to Tube 1 and left to separate at 20°C for ½ hour to simulate the normal lowest evaporator temperatures in residential air conditioning units. Tube 2 is cooled to <-50°C. After ½ hour at -20°C the toggle valve is opened and the bottom phase is transferred to tube 2. The lower phase is transferred due to the pressure/temperature differential between Tube 1 and 2.

The total mass of each phase is then calculated. The refrigerant is boiled off and the mass of oil in each phase is calculated. The lubricant fraction from each phase was submitted for analysis of weight % ester in AB. From this data the following phase composition Figures 1-4 were generated.

It can be seen from the upper phase graphs, Figures 2 and 4, that the amount of R407C (A/C9000) saturates at 30-40% with 20% POE in the blend. Further

increase in the amount of POE does not solubilize more refrigerant into the upper phase mixture (see Figure 4).

Alkylb nzen /Polyol st r Bl nds – Physical Data

From the above Examples, it was determined that from a cost and solubility/viscosity parameter the most suitable blends are 20 to 30 wt% POE in 70 to 80 wt% AB. The physical data on four such blends are shown in Table IV which provides the kinematic viscosity (kV) at 40 and 100°C, the viscosity index (VI), Total Acid Number (TAN) and pour point.

Table IV

Physical Data

Test	Units	ISO 32		ISO 68	
		80AB/20POE	70AB/30POE	80AB/20POE	70AB/30POE
KV, 40°C	CSt	26.2	26.4	52.1	52.6
KV, 100°C	CSt	4.3	4.4	5.9	6.1
VI		43	54	23	36
TAN	MgKOH/g	0.05	0.05	0.05	0.05
Pour Point	°C	-45	-51	-36	-39
T Number		T10540/96	T10541/96	T10652/96	T10653/96

Example 3:

Wear Data

The wear data shown in Table V was generated from Institute of Petroleum test number 239 4-ball test. A brief description of the test conditions for IP 239 are as follows:

Three balls are placed into a cup and secured with a clamping ring. The ball specimens are a chrome alloy steel of 12.7 mm diameter. Sample lubricant (8-10 ml) is poured into the cup in amount sufficient to cover the balls to a depth of at least 3 mm. A clean ball is fitted into the upper ball chuck and the chuck is fitted into the taper at the end of the motor spindle. The cup sits on a disk so it is free to rotate and the three balls in the cup are in contact with the fourth ball in the form of a pyramid. A load is applied and the ball cup rotates under the forth ball for a designated length of time. In this particular wear test several parameters were tested -- The mean wear scar diameter (MWSD), Initial Seizure Load (ISL) and the Weld Point. The MWSD

was taken after 1 hour with a 30 kg load. MWSD is the mean of six wear scar diameter measurements; two from each of the 3 stationary balls, taken in the direction of rubbing and at a right angle to this. The initial seizure load (ISL) is the lowest load at which seizure occurs and is measured in kilograms. Seizure indicates localized fusion of metal between the rubbing surfaces of the test pieces. Finally, the weld point is the load in kilograms at which the balls bond to each other. For each test a new set of four balls was used. The results are in the following Table V.

Table V

IP 239 4-Ball Test

Test	ISO 32		ISO 68	
	80/20	70/30	80/20	70/30
MWSD in mm at 1hr, 30kg	1.479	1.282	0.721	0.867
ISL, kg	40	35	40	40
Weld Pt, kg	120	130	120	130
T Number	T10540/96	T10541/96	T10652/96	T10653/96

SRV Ball on Disk Test

An Optimol® SRV oscillating-type wear-testing machine was used for the SRV Extreme Pressure (EP) Step test. In this machine the sliding system consists of an oscillating upper specimen and a stationary lower specimen. A ball of 10 mm in diameter is rigidly secured into the upper specimen holder. The ball slides over the disk specimen, which is rigidly secured in the lower specimen holder, giving the load in contacted state. The load and friction force are measured using a two-phase piezoelectric-type transducer. Friction coefficient is averaged over each period of oscillating run and recorded continuously. The ball and disk specimens were made of SUJ 2 (AISI 52100) bearing steel. The test conditions were as follows: The stroke length was 1 mm; the frequency was 50 Hz; and the initial load was 50 N. After 2 minutes the load was increased to 100 N. After each two minute interval the load was increased by 100 N to a maximum of 1400 N. The coefficient of friction was monitored continuously throughout the test. If the coefficient of friction is greater than 0.35 for more than 30 seconds, the test is automatically terminated. If the coefficient of friction does not exceed this value then the test will be run for 30 minutes by which time the maximum load is reached. The graph depicting the

coefficient of friction is shown in Figures 5-8. The length and width of the wear scars determined under an optical microscope are shown in Table VI.

In a second test, SRV 5AE Test, the ball was made of Aluminum 380. The stroke length was 1 mm; the frequency was 50 Hz; and the initial load was 50 N. The initial load was increased over 30 seconds to 300 N and maintained for the entire 2 hour test period. The coefficient of friction is measured continuously and shown in Figures 9-12. The length and width of the wear scars determined under an optical microscope are shown in Table VI.

Table VI

SRV Test	ISO 32		ISO 68	
	80/20	70/30	80/20	70/30
	Scar length and width in millimeters			
EP Test: Steel/Steel	0.90 x 1.06	0.93 x 1.11	0.77 x 0.98	1.17 x 1.10
5AE: Steel/Aluminum	1.00 x 1.00	1.50 x 0.50	0.88 x 1.02	1.53 x 1.50
T Number	T10710/96	T10711/96	T10712/96	T10653/96

Example 3 demonstrates that the products perform satisfactorily in all the wear tests and in terms of physical requirements.

The above Examples demonstrate that it is possible to solubilize HFC refrigerant into AB lubricant by the addition of POE to the AB. Addition of 20 to 30% by weight of POE to AB provides a considerable increase in HFC R407C solubility in lubricant phase over AB alone. This effect lowers the viscosity with the potential to give satisfactory oil return to the compressor.

The products have satisfactory physical and wear characteristics and are potential low cost alternatives to POE lubricants for use with HFC R407C in residential and commercial air conditioning applications.

<u>Example 4:</u> Sealed Tube Testing

Samples of 70 wt% AB and 30 wt% POE at viscosities ISO 32 (BXL-640) and ISO 68 (BXL-604) were blended and sent to an outside laboratory for sealed tube testing with refrigerant R410A in a 1:1 weight ratio. As shown in Table VII, neither lubricant showed signs of reaction in the presence of copper, iron and aluminum

when aged for 14 days at 175°C. Table VIII shows the Total Acid Number (TAN) values of both samples in a non-reacted (before sealed tube test) and reacted (after sealed tube test of 14 days at 175°C) state. The data in Tables VII and VIII show that the samples are thermally stable in the presence of refrigerant R410A.

Table VII

Lubricant	Days	Aluminum	Copper	Valve Steel	Lubricant
(BXL-604) ISO68	3	No reaction	No reaction	No reaction	Clear
	7	No reaction	No reaction	No reaction	Clear
	14	No reaction	No reaction	No reaction	Clear
(BXL-640) ISO32	3	No reaction	No reaction	No reaction	Clear
	7	No reaction	No reaction	No reaction	Clear
	14	No reaction	No reaction	No reaction	Clear

Table VIII

Lubricant	Reacted / Unreacted	Total Acid Number (mg KOH / g lubricant)
BXL-604	Unreacted	0.08
	Reacted	0.42
BXL-640	Unreacted	0.02
	Reacted	0.06

Example 5:

Lubricant profiles were conducted on BXL640 (ISO 32) and compared to Castrol Icematic® SW 32 polyol ester lubricant available from Castrol Industrial North America Inc, Downers Grove, IL. As shown in Figures 13-17 the pressure-temperature, solubility, viscosity-temperature, density-temperature and the Daniel

Plot diagrams all show that the blends of the present invention have similar profiles to that of 100% POE and are thus commercially acceptable.